Local fluctuations in the aging of a simple glass

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The presence of *dynamical heterogeneities*, i.e. nanometer-scale regions containing molecules rearranging cooperatively at very different rates compared to the bulk [3, 4], is increasingly being recognized as crucial in our understanding of the glass transition, from the non-exponential nature of relaxation, to the divergence of the relaxation times [5]. Recently, dynamical heterogeneities have been directly observed experimentally [6, 7, 8, 9] and in simulations [13]. However a clear physical picture for the origin of these heterogeneities is still lacking. Here we investigate a possible physical mechanism for the origin of dynamical heterogeneities in the non-equilibrium dynamics of structural glasses. We test the predictions regarding universal scaling of fluctuations derived from this mechanism against simulation results in a simple binary Lennard-Jones glass model, and find that to a first approximation they are satisfied. We also propose to apply the same kind of analysis to experimental data from confocal microscopy in colloidal glasses.

Supercooled liquids approaching the glass transition display increasingly slow dynamics, until eventually they cannot equilibrate in laboratory timescales [1]. One consequence of this fact is *physical aging*, i.e. the breakdown of *time translation invariance* (TTI): the correlation $C(t, t_w)$ between spontaneous fluctuations of an observable at times t (the final time) and t_w (the waiting time) are nontrivial functions of t and t_w, as opposed to being functions of the time difference $t - t_w$. In many cases, the two-time correlation $C(t, t_w)$ in an aging system separates into a fast, time translation invariant contribution $C_{\text{fast}}(t - t_w)$, and a slow contribution $C_{\text{slow}}(t, t_w)$ [2]: $C(t, t_w) = C_{\text{fast}}(t - t_w) + C_{\text{slow}}(t, t_w)$. In the case of a structural glass, two-step relaxation is observed: the fast term corresponds to localized fluctuations of individual particles inside their cages, and the slow term corresponds to longer time scales, in which cages break down and the system structurally relaxes. For some systems, the slow part of the correlation has the form [2] $C_{\text{slow}}(t, t_w) = C_{\text{slow}}(h(t)/h(t_w))$, where $h(t)$ is some monotonically increasing function. For example, in the case of domain growth, $h(t)$ is proportional to the domain size [2].

Recently, it has been proven that, in the limit of long times, the dynamics of a class of spin-glass models is invariant under *global* reparametrizations $t \to h(t)$ of the time [10]. This result has been used to predict the existence of a Goldstone mode in the nonequilibrium dynamics, associated with smoothly varying local fluctuations in the reparametrization of the time $t \to h_r(t) = e^{\varphi_r(t)}$. These fluctuations have been physically interpreted to represent local fluctuations of the age of the sample [11, 12]. In the cases where the *global* two-time correlation exhibits $h(t)/h(t_w)$ scaling, a simple Landau theory approximation for the dynamical action predicts [11, 12, 14] that the full probability distribution $\rho(C_r(t, t_w))$ of *local* correlations $C_r(t, t_w)$ depends only on the global correlation $C_{\text{global}}(t, t_w)$. In all of this discussion, only the slow part of the correlation is considered, and any effects due to the fast part of the dynamics are neglected.

In this Letter, we examine whether this theoretical picture can be extended to explain dynamical heterogeneities in the aging of structural glasses, by presenting the first detailed characterization of the behavior of fluctuations in the aging of a continuous-space, quasi-realistic structural glass model. The presence of a global symmetry under time reparametrization in the generating functional for the dynamics has been proven only for a class of spin glass models, and it is far from obvious whether it applies in off-lattice, quasi-realistic models, describing structural glasses. Addtionally, the question about the aging behavior of local observables in structural glasses remains mostly open. Almost all simulations in glass forming liquids have focused on the (equilibrium) supercooled liquid [13], although there are some recent results for kinetically constrained spin models of glassyness [14], and an earlier work exploring dynamic spatial correlations for soft spheres in the aging regime [15].

We probe individual particle displacements along one direction $\Delta x_j(t, t_w) = x_j(t) - x_j(t_w)$ (where j is the particle index); and also *local, coarse-grained* two-time functions: the correlator

$$C_{\mathbf{r}}(t, t_w) = \frac{1}{N(B_{\mathbf{r}})} \sum_{\mathbf{r}_j(t_w) \in B_{\mathbf{r}}} \cos(\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(t_w))), \quad (1)$$

and the mean square displacement

$$\Delta_{\mathbf{r}}(t, t_w) = \frac{1}{N(B_{\mathbf{r}})} \sum_{\mathbf{r}_j(t_w) \in B_{\mathbf{r}}} (\mathbf{r}_j(t) - \mathbf{r}_j(t_w))^2. \quad (2)$$

Here we consider a coarse graining cubic shaped box $B_{\mathbf{r}}$ of side ℓ around the point $\mathbf{r}$ in the system, and the sums run over the $N(B_{\mathbf{r}})$ particles *present at the waiting time* t_w in the box $B_{\mathbf{r}}$. We choose a value of q that corresponds to the main peak in the structure factor $S(q)$ of the system, $q = 7.2$ in Lennard-Jones units.

These definitions are inspired by the analogous definitions in the case of spin glasses [11, 12], and *can be applied both to analyze data obtained from simulations and from confocal microscopy experiments*. The *global* quantities $C_{\rm global}(t, t_w)$ (incoherent part of the intermediate scattering function) and $\Delta_{\rm global}(t, t_w)$ (mean square displacement) are defined by extending the sum to the whole system in Eq. (1) and Eq. (2) respectively.

We performed 250 independent molecular dynamics runs for the binary Lennard-Jones (LJ) system of Ref. [16], which has a mode coupling critical temperature $T_c = 0.435$. A system of 8000 particles was equilibrated at a temperature $T_0 = 5.0$, then instantly quenched to $T = 0.4$, and finally it was allowed to evolve for 10^5 Lennard-Jones time units. The origin of times was taken at the instant of the quench.

As mentioned above, we want to test whether the probability distributions of local correlations depend on the two times t, t_w only through the values of a global correlation. Unlike in spin systems, in the case of a structural glass there are different global correlation functions associated with the microscopic degrees of freedom in the system, including the self-intermediate scattering function $C_{\rm global}(t, t_w)$ and the mean square displacement $\Delta_{\rm global}(t, t_w)$. This leads us to testing two possible hypothesis: a) that the probability distributions coincide when $C_{\rm global}(t, t_w)$ is kept constant; and b) that the probability distributions coincide when $\Delta_{\rm global}(t, t_w)$ is kept constant. Extensive checking of our numerical data indicates that a) is approximately satisfied by the probability distributions of $C_r(t, t_w)$, $\Delta_{\mathbf{r}}(t, t_w)$ and $\Delta x(t, t_w)$, but b) is satisfied only to a much lesser degree [17].

In Fig. 1 we present our results for the probability distribution $\rho(C_r(t, t_w))$ of the local intermediate scattering function for waiting times $t_w = 30.20, \cdots, 30200$, and final times t chosen so that $C_{\rm global}(t, t_w) \in \{0.1, 0.3, 0.5, 0.7\}$. We observe that the data approximately collapse for each value of $C_{\rm global}(t, t_w)$. This kind of collapse is also observed in simulations in a 3D spin glass model, but in the case of the spin glass model, the collapse is more precise than here. Unlike the case of the 3D spin glass model, the position of the peak in the distribution $\rho(C_r)$ is strongly dependent on the value of $C_{\rm global}(t, t_w)$. The skewness of $\rho(C_r)$ also depends dramatically on $C_{\rm global}(t, t_w)$: it goes from highly skewed for $C_{\rm global}(t, t_w) = 0.7$ to almost symmetric around its peak for $C_{\rm global}(t, t_w) = 0.1$. As shown in the figure, the distributions $\rho(C_r(t, t_w))$ for $C_{\rm global}(t, t_w) = 0.1$ can be well approximated by a Gaussian fit, but this does not hold for larger values of $C_{\rm global}(t, t_w)$. Unlike previous results

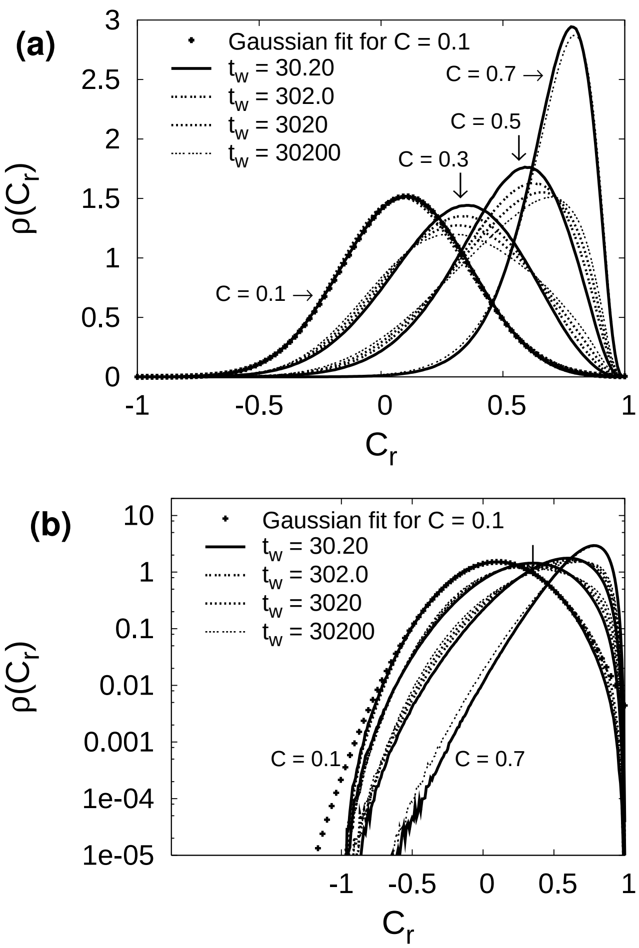

FIG. 1: Probability distributions $\rho(C_r(t, t_w))$ for values t_w in the range 30.20 – 30200 (as indicated by the key in the figure), plotted for final times t chosen so that $C_{\rm global}(t, t_w) \in \{0.1, 0.3, 0.5, 0.7\}$. Coarse graining box size $\ell \approx 0.11L$, (with $L \equiv$ linear size of the simulation box). The curves collapse into four groups, corresponding to $C_{\rm global} = 0.7, 0.5, 0.3, 0.1$ (ordered from highest to lowest value of C_r at the peak). A gaussian fit to the data for $C = 0.1$ is also shown. Top panel: linear scale. Bottom panel: logarithmic scale.

in kinetically constrained models [14], in the present case, Gumbel distributions *do not* provide good fits to $\rho(C_r)$. To characterize the weak dependence of the probability distributions on waiting time at fixed $C_{\rm global}(t, t_w)$, in the top panel of Fig. 3 we plot the centered second moment of the distributions $\rho(C_r)$ as a function of waiting time, for fixed $C_{\rm global}(t, t_w) \in \{0.1, 0.3, 0.5, 0.7\}$. The dependence on t_w is so weak that both a logarithmic form and a power law form (with powers in the range $0.01 - 0.07$) provide a good fit.

In Fig. 2 we present our results for the probability distribution $\rho(\Delta x(t, t_w))$ of the particle displacements $\Delta x_j(t, t_w) = x_j(t) - x_j(t_w)$ along one direction. In the top panel of Fig. 2 we can observe that these data also

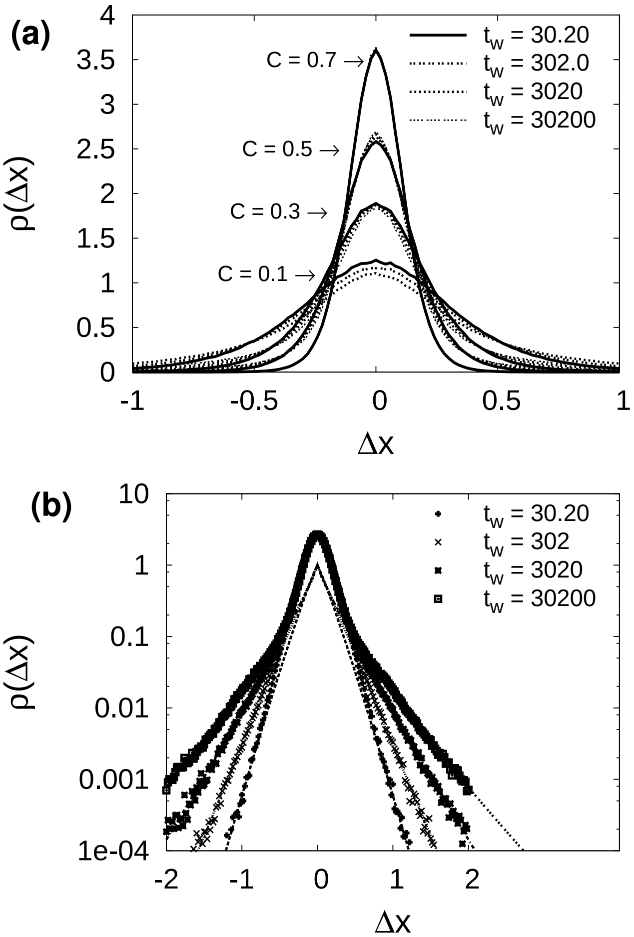

FIG. 2: Top panel: Probability distributions $\rho(\Delta x(t, t_w))$ for values t_w in the range 30.20 – 30200 (as indicated by the key in the figure), plotted for final times t chosen so that $C_{\rm global}(t, t_w) \in \{0.1, 0.3, 0.5, 0.7\}$. The curves collapse into four groups, corresponding to $C_{\rm global} = 0.1, 0.3, 0.5, 0.7$ (ordered from lowest to highest value of $\rho(\Delta x)$ at the peak). Bottom panel: Tails of the distributions $\rho(\Delta x(t, t_w))$, for $C = 0.5$ and $t_w = 30.20, 302, 3020, 30200$ (from narrower to wider tail). Symbols: results from simulation. Lines: fits to the data for $|\Delta x| > 0.5$ using a stretched exponential form $\rho(\Delta x(t, t_w)) \approx \mathcal{N} \exp(-|\Delta x/a|^\beta)$, with exponents $\beta = 1.11, 1.01, 0.90, 0.81$ respectively.

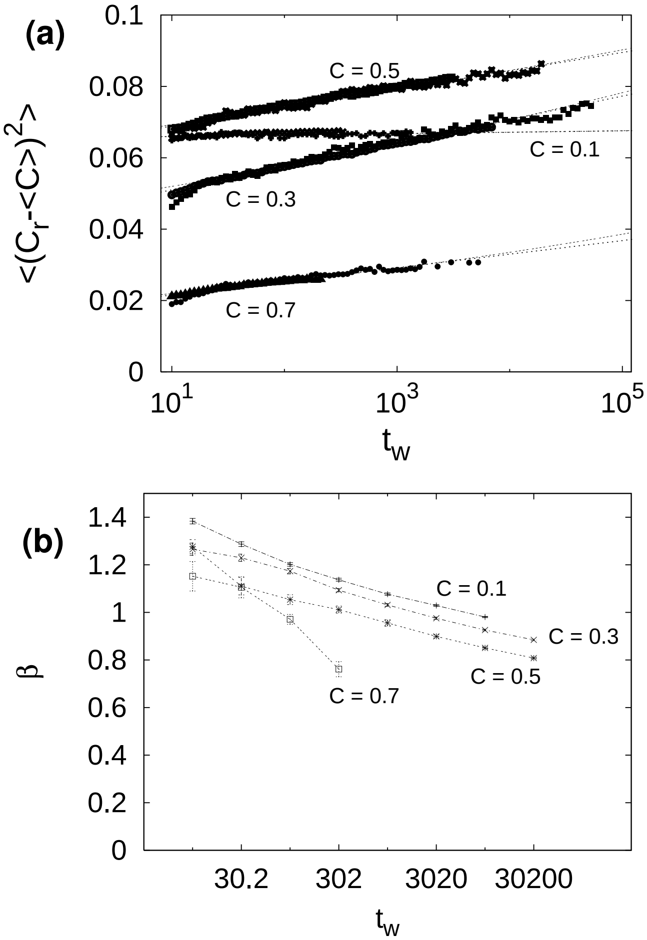

FIG. 3: Evolution of the probability distributions, as a function of the waiting time t_w, at constant $C_{\rm global}(t, t_w) \in \{0.1, 0.3, 0.5, 0.7\}$. Top panel: second moment of $\rho(C_r(t, t_w))$, together with fits to the functional forms: $m_0(t_w)^a$ (full lines) and $m_0' \log(t_w/t_0)$ (dotted lines). Bottom panel: stretching exponent β for the tails of $\rho(\Delta x)$, as a function of the waiting time t_w, at constant $C_{\rm global}(t, t_w) \in \{0.1, 0.3, 0.5, 0.7\}$ (the lines are only guides to the eye).

approximately collapse for each value of $C_{\rm global}(t, t_w)$. In the bottom panel we have a closer look at the tails of $\rho(\Delta x(t, t_w))$. We find that the distribution is non-gaussian, as was observed in experiments in colloidal glasses in the supercooled regime [7]. The tails of the distribution can be fitted with a stretched exponential form $\rho(\Delta x) \approx \mathcal{N} \exp(-|\Delta x/a|^\beta)$, and they become more prominent as t_w grows (for constant $C_{\rm global}(t, t_w)$). Indeed, as shown in the bottom panel of Fig. 3, the exponent β decreases from values above unity at short waiting times t_w to values of around 0.8 at much longer t_w.

To summarize, in this Letter we have presented the first detailed characterization of non-equilibrium fluctuations in the aging regime in a continuous-space, quasi-realistic structural glass model. It is also the first test for the possible presence in such models of a Goldstone mode associated with reparametrizations of the time variable, which could explain the behavior of fluctuations in the aging regime. We have found that, as expected from the Goldstone mode picture, the probability distributions for the local fluctuating two-time quantities are, to a first approximation, invariant when the global intermediate scattering function $C_{\rm global}(t, t_w)$ is kept constant.

Besides the scaling predicted by the Goldstone mode picture, a detailed analysis of the probability distri-

butions for local observables uncovers that: i) unlike the case of spin glasses, the position of the peak for the probability distributions of the local correlation $\rho(C_r(t,t_w))$ shifts dramatically as a function of the value of $C_{\rm global}(t,t_w)$; ii) the distribution $\rho(C_r(t,t_w))$ evolves gradually from being highly skewed and non-gaussian for larger values of $C_{\rm global}(t,t_w)$ to being unskewed and very close to gaussian for small values of $C_{\rm global}(t,t_w)$; iii) a more detailed examination of the probability distributions at constant $C_{\rm global}(t,t_w)$ reveals that the moments of the distributions evolve smoothly as a function of the waiting time t_w, without displaying any obvious characteristic timescale (this may be due in part to the fact that the dynamic correlation length in the system is growing as a function of t_w, but for the timescales of the simulation it is not yet larger than the size of the coarse graining box used [18], leading to a gradual increase in the variance of all coarse grained quantities) ; iv) the probability distributions of one-dimensional displacements $\rho(\Delta x(t,t_w))$ are clearly non-gaussian, as in confocal microscopy experiments *in the supercooled liquid* regime [7], and their tails can be fit by stretched exponential forms, with exponents β that decrease from $\beta > 1$ to $\beta \approx 0.8$ as t_w increases (for fixed $C_{\rm global}(t,t_w)$).

We conclude that the probability distributions of local observables in the aging regime are consistent with the presence of a Goldstone mode controlling the nonequilibrium dynamics of a structural glass. We suggest that a direct experimental test of this picture could be provided by applying a similar analysis to experimental data from confocal microscopy in colloidal glass systems.

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